ESTERIFICATION OF OLEIC ACID WITH ETHANOL BY USING SULFATED ZIRCONIA CATALYST IN THE PRESENCE OF TRIGLYCERIDES: KINETIC AND MODELING STUDY

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A thesis submitted in fulfilment of the requirement for the award of the degree of Bachelor of Chemical Engineering

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I declare that this thesis entitled "*Esterification of Oleic Acid With Ethanol by Using Sulfated Zirconia Catalyst in The Presence of Triglycerides: Kinetic and Modeling Study*" is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree."

Signature **:……**

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Date **: 20th APRIL 2009**

Special Dedication of This Grateful Feeling to My…

Beloved parent;

Mr. Mohamad Yazid b. Abu Yamin & Mrs. Norhaini bt. Timin

For Their Love, Support and Best Wishes.

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ABSTRACT

This dissertation is about the esterification of oleic acid with ethanol by using sulfated zirconia as a catalyst in the presence of triglycerides. In this dissertation the kinetic and the modeling study about the reaction as well as the best operating parameter for the reaction will be studied and investigated. Biodiesel is the one the new possible substitute of regular fuel for engines and it can be produced from various animal fats and vegetable oils. The biodiesel has more advantages compared to the fossil based fuel because it has lower emission of carbon monoxide due to the better combustion, a better lubricating effect on engines, non sulfur emission and non particulate matter pollutant. In this study, there are four operating parameter were investigated and studied which are temperature, amount of catalyst, ratio of oleic acid to the ethanol and the addition of triglycerides. The best operating condition in this study has been produced 31.7% final conversion of oleic acid. The experimental data have been interpreted with pseudo-homogenous kinetic model and the rate constant has been determined from the calculation. It was found out that the sulfated zirconia catalyst was suitable to perform not only esterification reaction but also the tranesterification reaction in biodiesel production.

ABSTRAK

Disertasi ini adalah berkenaan pengesterifikasian asid oleik dengan etanol menggunakan “sulfated zirconia” sebagai pemangkin dengan kehadiran “triglycerides”. Di dalam disertasi ini, model kinetik dan juga pemodelan tindak balas disertai parameter operasi untuk tindak balas akan dipelajari dan disiasat. Biodiesel adalah satu sumber tenaga yang berpontensi untuk menjadi alternatif untuk digunakan di dalam enjin dan ia juga boleh dihasilkan dari pelbagai lemak haiwan dan minyak sayuran. Biodiesel mempunyai pelbagai kelebihan berbanding minyak bersumberkan fosil antaranya mengeluarkan karbon monoksida yang sedikit disebabkan pembakaran yang lebih sempurna,pelincir enjin yang efektif, tiada pelepasan sulfer dan tidak menghasilkan bahan yg mencemarkan alam. Di dalam kajian, terdapat parameter operasi yang diambil kira iaitu suhu, amaun pemangkin, nisbah asid oleic kepada alkohol dan juga penambahan “triglycerides”. Kombinasi operasi parameter yang terbaik telah dapat menghasilkan penukaran asid oleik kepada ester sebanyak 31.7%. Data eksperimen telah dianalisis kepada bentuk model “pseudo-homogenous” dan kadar tindakbals telah diketahui melalui pengiraan yang dilakukan. Maka, telah diketahui bahawa pemangkin sulfated zirconia adalah sesuai digunakan dalam “esterification” dan juga “transesterification” di dalam penghasilan biodiesel.

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CHAPTER 1

INTRODUCTION

1.1 Background

In 1900, Rudolf Diesel demonstrated his compression ignition engine at the World's Exhibition in Paris. In that prototype engine, he used peanut oil which is the first biodiesel. Vegetable oils were used until the 1920's when an alteration was made to the engine for enabling it to use a residue of petroleum diesel. Although the diesel engine gained worldwide acceptance, biodiesel did not. With affordable price, availability, and government subsidies, petroleum diesel quickly became famous for the diesel engine.

In the mid 1970s, fuel shortages revived interest in developing biodiesel as an alternative to petroleum diesel. However, as the petroleum market was increasingly subsidized, biodiesel was again downgraded to a minority alternative status. This political and economic struggle continues to limit the impact of the biodiesel industry today.

Now, increasing concerns about the potential of global climate change, declining air and water quality, and serious human health concerns are inspiring the development of biodiesel. Biodiesel is made from recycled vegetable oil and various feedstock as for example soya beans. As part of an active carbon cycle biodiesel feedstock production reduces the buildup of greenhouse gases, and in turn, global warming.

Many fleet operators have made the switch to biodiesel, yet biodiesel consumption accounts for less than one percent of the total diesel fuel consumption in the United States. Additional industries finding cleaner alternatives to sulfur emitting diesel are transit bus fleets, heavy-duty truck fleets, airport shuttles, marine and national park boats and vehicles, mining, the military and many more.

Biodiesel as the one of the ester has been increasingly produced recently. The advantages of using this fuel are lower the emission of carbon monoxide (CO) due a better combustion, a better lubricating effect on engines, non sulfur emission and non particulate matter pollutant. Biodiesel can be produced by esterification of free fatty acid with alcohol to form an ester and water.

Usually, this biodiesel is synthesized using homogenous acid-catalyzed system like sulfuric acid and hydrochloric acid as catalyst. But this system has a drawback as the separation process is needed in order to separate homogenous catalyst from the ester. It is good way to use solid acid catalyst because it makes less harm to the environment compared to the homogenous system. Furthermore, the process complexity of the system can be reduced since there is no separation process involved in the system. By other means, less money spent will be required to setup this system.

The function of catalyst used in the reaction is mainly to reduce the activation energy of the reaction so less time is required to achieve high conversion. There are many type of catalysts that are suitable for the esterification reaction, these catalysts are ion exchange resin, zeolite, and superacid like sulfated zirconia and tungstated zirconia.

There is another method to produce biodiesel like transesterification. Transesterification, also called alcoholysis, is the displacement of alcohol from an ester by another alcohol in a similar to hydrolysis, except than alcohol is used instead of water (Song et al., 2007). But this kind of reaction has disadvantages as the reaction can be reversible and the reaction time take much longer compared to the esterification.

1.2 Identification of problem

The use of solid acid catalyst in biodiesel applications has gained attention in recent years. The problem we are facing right now, even though these acid solid catalysts are effective in esterefication and transesterification but it required high temperature condition to achieved high conversion compared to base catalyst (Furuta et al., 2004). Some resins, such as Amberlyst-15, may be considered an exception as these catalysts catalyze appreciably both esterification and transesterification reactions under mild reaction conditions due to their high concentrations of acid sites (Lo´pez et al., 2005). However, thermal stability becomes an issue when resin-type catalysts are used at higher temperatures (for higher reaction rates, reactive distillation applications, or catalyst regeneration). In this study, the catalytic performance of thermally robust sulfated zirconia will be investigated. In order to produce a large scale of biodiesel production, an appropriate kinetic model must be chosen and developed first. The important of developing kinetic model before design a reactor is to ensure that the design of reactor satisfied with the optimum condition. There are many kinetic models that can be chosen such as pseudo-homogenous model, Langmuir-Hinshelwood model and Langmuir-Hinshelwood-Hougen-Watson model.

1.3 Statement of objectives

1. To study the effect of important operating parameters to the rate of reaction.
2. To develop a kinetic model for the fatty acid esterification reaction.

1.4 Scope of study

In this study, four parameters were investigated. These parameters are temperature, amount of catalyst, amount of triglycerides, and ratio of alcohol to acid. The selected temperature is 35°C, 45°C and 55°C. For the amount of catalyst, the amount used is 0.5gram, 1 gram and 1.5 gram. The ratio of acid to alcohol in this study is 1:1, 1:2 and 1:4. For the forth parameter which is amount of triglycerides, the amount used is 10 ml, 20 ml and 30 ml. Oleic acid and ethanol were used as the reactant and sulfated zirconia acted as a catalyst. The data obtained from the experiment was analyzed and fitted into an appropriate heteregenous kinetic model.

1.5 Rationale and significance

Due to the decreasing of the resource of fossil based fuel, the demand for the alternative fuel was increased. The objective for this research is to find the kinetic model for the esterification reaction which is useful for industries that want to construct a biodiesel reactor. Other than that, this renewable energy can reduce the pollution due to the lower emission of carbon moxide. This advantage can attract many people to invest to commercialize this biodiesel. In addition, the source for biodiesel is easy to get since the source come from vegetable oil and animal fat that can be renewable. It also good opportunity for agriculture and rural economies since it can generate more profit and contribute more job opportunity to that sector.

CHAPTER 2

LITERATURE REVIEW

2.1 Biodiesel

Biodiesel is a fuel comprised of alkyl esters of long chain fatty acids (Van Gerpen et al., 2004). It is an alternative way to reduce emission of carbon monoxide (CO) and sulfur dioxide (SO_2). The composition of biodiesel is similar to petroleum based diesel so it can replace petroleum based diesel completely or can be blend with petroleum base diesel. Besides, the biodiesel production can give social impact to the country that their economy is base on agriculture. There are two ways to produce biodiesel which are esterification or transesterification reaction.

2.2 Esterification

Esterification is the general name for a chemical reaction in which two reactants typically an alcohol and an acid form an ester as the reaction product. Esters are common in organic chemistry and biological materials, and often have a characteristic pleasant, fruity odor. This leads to their extensive use in the fragrance and flavor industry.

Esterification is a reversible reaction. Hydrolysis involves adding water and a catalyst commonly NaOH to an ester to get the sodium salt of the carboxylic acid and alcohol. As a result of this reversibility, many esterification reactions are equilibrium reactions and therefore need to be driven to completion according to Le Chatelier's

principle. Esterifications are among the simplest and most often performed organic transformations.

A common type of esterification is a Fischer esterification. In the Fischer esterification, esters may be prepared by refluxing an acid (usually, but not always a carboxylic acid) and a primary or secondary alcohol in the presence of a catalyst (commonly concentrated sulfuric acid). Water is a byproduct, and it can be removed to force the equilibrium in the desired direction. Alternatively, where the ester has a suitable boiling point, it may be distilled off, once again causing the equilibrium to favor the product.

For example, esterification of acetic acid in excess ethanol possibly as the solvent in the presence of concentrated sulfuric acid as a catalyst results in an ester (ethyl acetate). Figure 2.1 shows the general esterification process.

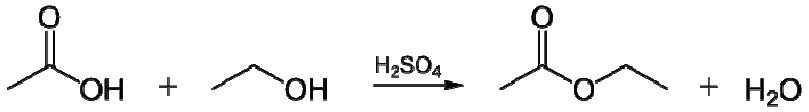

Figure 2.1 Esterification reaction

2.3 Transesterification

In organic chemistry, transesterification is the process of exchanging the alcohol group of an ester compound with another alcohol. These reactions are often catalyzed by the addition of an acid or base. Acids can catalyse the reaction by donating a proton to the carbonyl group, thus making it more reactive, while bases can catalyse the reaction by removing a proton from the alcohol, thus making it more reactive.

Transesterification is used in the synthesis of polyester, in which diesters undergo transesterification with diols to form macromolecules. For example,

dimethyl terephthalate and ethylene glycol react to form polyethylene terephthalate and methanol, which is evaporated to drive the reaction forward. The reverse reaction (methanolysis) is also an example of transesterification, and has been used to recycle polyesters into individual monomers. Figure 2.2 shows the general transesterification process.

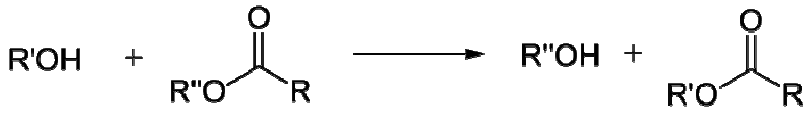

Figure 2.2 Transesterification reaction

Transesterification also has been used for producing biodiesel long time ago. There is method called supercritical process which is catalyst free method for transesterification uses supercritical methanol at high temperatures and pressures in a continuous process. In the supercritical state, the oil and methanol are in a single phase, and reaction occurs spontaneously and rapidly. The process can tolerate water in the feedstock and free fatty acids are converted to methyl esters instead of soap, so a wide variety of feedstock can be used. Also the catalyst removal step is eliminated. High temperatures and pressures are required, but energy costs of production are similar or less than catalytic production routes. Vera et al. (2006) in their research of production of biodiesel by a two-step supercritical reaction process with adsorption refining, they were compared to the production of biodiesel by using one step supercritical reaction process. They were found out that the operating pressure for the production of biodiesel by the reaction of oils in supercritical methanol can be advantageously reduced if the reaction is allowed to proceed in two successive steps with intermediate removal of glycerol. The one-reactor setup works with molar methanol:oil=42 and a pressure of 14-43 MPa (270-350°C). In the two-reactor setup the decrease of methanol:oil to 10 results in a reduction of the working pressure toless than 4 MPa and of the pumping power to less than 25% the value for the one-reactor lay-out.

A low methanol:oil ratio also enables the use of adiabatic flash drums to vaporize the unreacted methanol at the outlet of the reactor, with a substantial decrease of the heat duty of the process. An additional heat exchanger contacting the streams entering and exiting the reactor enables an additional recovery of heat. The final heat duty can be reduced to almost half the value corresponding to the one-reactor lay-out with no heat recovery and no methanol removal.

The supercritical catalyst-free process can be run under fully dry conditions if glycerol removal is performed by adsorption in a packed bed. Common acid adsorbents (silica, acid resins) can retain glycerol and keep the biodiesel product inside the glicerol content specification of the quality norms. A convenient regeneration procedure seems to be the flushing of the adsorbed glycerol with a methanol stream and the recycling of this stream to the first supercritical reactor. Figure 2.3 shows the flowsheet of two step supercritical biodiesel production process.

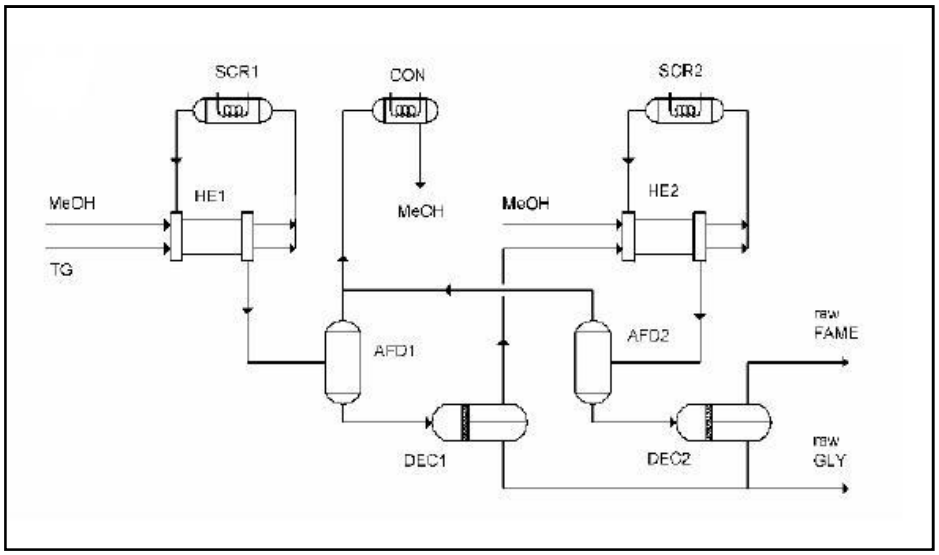

Figure 2.3 Flowsheet of two step supercritical biodiesel production process

2.4 Type of catalyst

The esterification process can be homogenously or heterogeneously catalyzed. Homogenous esterification can be defined as the esterification process occurred in the same phase which is liquid-liquid phase between catalyst and the reactant. Meanwhile, the heterogenous esterification system occurred in liquid-solid phase.

Currently homogenous catalyst is in most used because it is cheaper as compared to the solid catalyst. Homogenous catalysts can be categorized into two types which are acid-catalyst and base-catalyzed. Most people more prefer to use homogenous acid catalyst since it is faster 4000 times than homogenous base catalyst (Lotero et al., 2005).

2.5 Homogenous catalyst

In the study of Donato et al. (2007), they tried to compare the performance of various homogenous acid catalysts such as sulfuric acid, methanesulfonic acid, phosphoric acid and trichloroacetic acid.

Sulfuric acid and methanesulfonic acid showed very promising result. These two catalysts have the conversion rate over 80%. But when sulfuric acid compared to the methanesulfonic acid in term of price and availability, sulfuric acid win in this situation. However, people concerned about these catalysts are they might be harmful to the environment if they are not treated carefully. Moreover, homogenous catalysts are hard to separate since the product has to undergo separation process because the product and the catalyst are mix together.

They have made a conclusion that small amount of catalyst (0.01% w/w) is enough to promote the reaction, with the conversion increasing with higher amounts of catalyst. Acid strength of the catalyst was responsible for the higher activity of sulfuric and methanesulfonic acids, releasing more H+ species to protonate the

carboxylic moiety of the fatty acid (rate determinant step). Shorter chain and higher polarity of methanol has resulted in higher activity than ethanol, which presents steric hindrance in the reaction and shows higher water inhibition, attributed to phase miscibility and emulsion formation. Kinetic parameters obtained were similar to the ones reported for transesterification reaction, indicating a similar rate determinant step. Lower activation energy was the exception. Quantum chemistry studies have shown that despite the similar protonation energy of fatty acid, the double bond of oleic acid increase the reactivity of carboxylic moiety of the fatty acid.

The other study of homogenous catalyst such as esterification of free fatty acids using sulfuric acid as catalyst in the presence of triglycerides (Marchetti and Errazu, 2007) they want to find the most optimum operating condition for this reaction. The final purpose for their study is to find the kinetic model for this esterification reaction. They have studied four parameters for the reaction between well mixed sunflower oil and oleic acid with ethanol. For the first parameter, ratio of alcohol to acid oil, they find out that when the molar ratio of alcohol to acid oil was low, the reaction occurred faster but reached a lower final conversion compared with when a higher molar ratio was used. In the latter case, the final conversion reached was higher, but the initial reaction rate was slow.

For the second parameter which is amount of catalyst, the result shown that the reaction was highly depend on the amount of catalyst. The effect of the catalyst just did to the initial rate but nothing effected to the final conversion of free fatty acid.

For the third parameter, which is temperature, they were expected that the temperature affected to the final conversion of free fatty acid. Their assumption seems true since the final conversion increased when the temperature increased.

The last parameter that they have investigated is the initial amount of free fatty acid. The result showed when the free fatty acid (FFA) amount increased the rate of reaction increased as well as final conversion.

In other research of homogenous catalyst acid which is esterification of free fatty acids (FFA) in sunflower oil with methanol in the presence of sulphuric acid (Berrios et al., 2007), they carried out the experiment sunflower oil mix with oleic acid with the methanol in the presence of sulphuric acid. The experimental results were found to fit a first-order kinetic law for the forward reaction and a second-order one for the reverse reaction. The influence of temperature on the kinetic constants was determined by fitting the results to the Arrhenius equation. The energy of activation for the forward reaction decreased with increasing catalyst concentration from 50745 to 44 559 J/mol. Based on the experimental results, a methanol/oleic acid mole ratio of 60:1, a catalyst (sulphuric acid) concentration of 5 wt% and a temperature of 60°C provided a final acid value for the oil lower than 1 mg KOH/g oil within 120 min. This is a widely endorsed limit for efficient separation of glycerin and biodiesel during production of the latter.

2.6 Heterogenous catalyst

Heterogenous catalysts now obtain many attentions from researchers around the world. They have performed many experiments to find most reliable and suitable catalyst to replace the homogenous catalyst which has some drawbacks. Many solid acid catalysts have been tested. These solid acid catalysts include ion-exchange resins (Altiokka et al., 2003), zeolites (Corma et al., 1989) and superacids like sulphated zirconia (Ardizzone et al., 1999) and niobium acid (Chen et al., 1984).

The esterification of free fatty acid and transesterificaton of vegetable oil with methanol has been carried out using Lewis solid acid but required high reaction temperature. Prior to that, the esterification of free fatty acid with methanol using solid acid catalyst in the reactor is a promising way to convert the reactant into valuable fatty acid methyl ester (FAME). Ni and Meunir (2007) in their experiment of esterification of free fatty acid in sunflower oil over solid acid catalyst using batch reactor have reported many aspects that affect the conversion rate of palmitic acid. They tested five catalysts which are sulfuric acid, silica alumina, tungstated zirconia, sulfated zirconia and SAC-13. The conversion of palmitic acid is measured at 60°C

over several of solid acid catalysts and acid sulfuric to investigate the optimum conversion of solid acid catalyst. The sulfated zirconia and SAC-13 give the best conversion rate over time but after consider the problem that sulfated zirconia had to activate above 400°C, the SAC-13 get advantage since it not required to be activated. One more problem that sulfated zirconia loss it weight due to the leaching of sulfate group. There is also probability the sulfated ziroconia cannot be recovered to the initial activity condition because of the formation of carbon residue derived from the decomposition of the oil absorbed on the material (Ni and Meunir, 2007).

Lopez et al. (2007) in his finding showed that the fresh sulfated zirconia was found to be the most active for the reaction among three catalysts he was used (titania zirconia, tungstenated zirconia, sulfated zirconia) in the experiment of esterification and transesterification using modified zirconia catalyst. But sulfated zirconia has a limitation since it cannot easy to regenerate. Titania zirconia has greater activation energy for tranesterification than tungstated zirconia. However they found that titania zirconia has weaker activation energy towards esterification. Thus, Lopez et al. (2007) suggested that tungstated zirconia is more suitable for the reaction since it is more active for the esterification than titania zirconia. This statement also has been strengthened by Park et al. (2008) in their study of heterogeneous catalyst using tungstated zirconia and sulfated zirconia. The sulfated zirconia and tungstated zirconia catalysts were found to be effective in the esterification of free fatty acid (FFA) to fatty acid methyl ester (FAME). However, sulfated zirconia was not selected because of the potential loss of sulfate ion (SO_4^{2-}) in its liquid-phase application. The pellet-type tungstated zirconia catalyst was used for the longer reaction test. The result showed that 65% conversion could be maintained for up to 140 hour. From the characterization results, the oxidation state of tungsten is mainly related to the catalytic activity of tungstenated zirconia. The activity could be regenerated through simple air re-calcination. The TPD results indicated that the surface acid strength was distributed widely. Moreover, there was a decrease in acidity with decreasing catalytic activity, which appears to be related to the oxidation state of the tungsten.

In the study of comparison of commercial solid acid catalysts for the esterification of acetic acid with butanol (Peters et al., 2005), they have been tested